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54) Method of recovery of dimethylterephthalate

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Specification.

1. Title of the invention.

Method of recovery of dimethylterephthalate.

2. What is claimed.

1. A method of recovery of dimethylterephthalate with the characteristic that a moulded product of a resin that contains polyester with polyethyleneterephthalate as the main component and polyamide with poly- $\epsilon$ -caproamide as the main component is depolymerized with methanol, and that subsequently, the dimethylterephthalate that is produced is isolated and recovered.

2. The method of recovery that has been described in § 1 of this claim with the characteristic that a moulded product of a resin is depolymerized with ethyleneglycol, and that then the ethyleneglycol ester of terephthalate that is produced and/or its oligomers are reacted with methanol.

3. The method of recovery that has been described in § 1 or § 2 of this claim with the characteristic that the content of the terephthalic acid component in the moulded resin product is at least 10 wt%.

3. Detailed description of the invention.

This invention pertains to a method of recovery of dimethylterephthalate. With more details, it pertains to a method of recovery of dimethylterephthalate from moulded products of resins that contain at least a terephthalic acid component and an  $\epsilon$ -caprolactam component.

The quantity of synthetic fiber products that is used in the world increases very rapidly, and will now be about 5000.000 tonnes/ annum. The consumption of such synthetic fiber products of course causes production of extremely large quantities of waste that originates in fiber products, and particularly in the cities of advanced countries and their surroundings, with a high number of inhabitants per unit of surface area and in addition a high consumption of such products per person, said waste is

coupled with various other wastes, and outdistances the increase of the capacity of waste treatment, and causes important social problems.

With respect to methods of recovery of dimethylterephthalate, that is useful for the industry, from such waste, in the past recovery from waste polyethyleneterephthalate has been widely investigated, but systems that contain a poly- $\epsilon$ -caprolactam component have absolutely not been investigated. The reason is that it is thought that when poly- $\epsilon$ -caprolactam is heated in the presence of alcohols, partial depolymerization and alkylation occur, and it is converted to oligomers that are soluble in alcohols, and that these are mixed with the dimethylterephthalate that is the aim, so that the decline of the quality thereof is remarkable.

It has to be considered, however, that the waste contains a fairly large quantity of poly- $\epsilon$ -caprolactam products, and in fact the separation and removal of poly- $\epsilon$ -caprolactam products from the waste is impossible, and discovery of the conditions of treatment of separation of the two of them would be very significant for the industry.

The present inventors paid attention to these problems, and achieved this invention with the discovery of a method for extremely simple recovery of dimethylterephthalate that is useful for the industry, with, as the raw material, fiber products and other products that are discarded by the household, industry, corporations and others, and that hitherto were incinerated as products without any value, and particularly synthetic fibers from moulded resin products that contain polyester with polyethyleneterephthalate as the main component and polyamide with poly- $\epsilon$ -caprolactam as the main component. That is to say that this invention is

1) a method of recovery of dimethylterephthalate with the characteristic that a moulded product of a resin that contains polyester with polyethyleneterephthalate as the main component and polyamide with poly- $\epsilon$ -caproamide as the main component, is depolymerized with methanol, and that subsequently, the dimethylterephthalate that is produced is isolated and recovered, and

2) is a method of recovery with the characteristic that the above mentioned moulded resin product is depolymerized with eth-

yleneglycol, and that then the ethyleneglycol ester of terephthalate that is produced and/or its oligomers are reacted with methanol, and that subsequently the dimethylterephthalate that is produced is isolated and recovered.

There are no special limitations with respect to the form of the resin moulded products that are the object of this invention, and they may by any of the so-called yarn, fibers, processed yarn, cord or fabric, knitted products, webbed products, knit-woven products or non wovens and sheet shaped products. Moreover, they may also be dresses and other products that have been produced therefrom.

Such moulded resin products may have, in their components, also homo- or copolymer moulded products of one or two or more components, and may also be a mixture of moulded products of compositions of homo- and copolymers.

The aim of this invention, however, is the recovery of dimethylterephthalate, and of course, moulded products that contain a terephthalic acid component, are the object of this invention.

At present, the synthetic fiber products that are in general sold commercially, often contain moulded products that consist of compositions with polyethyleneterephthalate as the main component, moulded products that consist of compositions with poly- $\epsilon$ -caproamide as the main component, and moulded products that consist of compositions with polyacrylamide as the main component, but the moulded resin products that are the object of this invention are those that contain at least 10 wt% or more, and preferably 20 wt% or more terephthalic acid component, as the acid, in the total weight, and still more preferred is the selection of moulded products that contain 30 wt% or more. Moreover, it is preferred that the quantity of  $\epsilon$ -caproamide is 5-50 wt%, and preferably 5-40 wt%.

The moulded resin products that are the object of this invention may contain, in addition to the above mentioned components, also components such as cotton, linen, acryl, polypropylene, polyethylene, nylon 66, and in addition rayon, acetate and polyvinylchloride etc. Moreover, the above mentioned moulded resin products may also be ones that contain various dyes, pigments, organic and inorganic additives, aftertreatment agents etc.

The main object of the above mentioned polyester is polyethylene terephthalate, but it may also be a product wherein a part of the terephthalic acid component and/or the ethyleneglycol component has been substituted by other dicarboxylic acids and/or glycol components, or wherein the polyamide component has been copolymerized. Moreover, the main object of the polyamide is poly- $\epsilon$ -caprolactam, but it may also be a product wherein a part of the  $\epsilon$ -caprolactam component has been substituted by other polyamide components or polyester components.

Because it is thought that the moulded resin products are polluted with oil or soil, it is prefered to remove such oil and soil in advance by rinsing with water etc. in the execution of this invention.

Moreover, because size, form and state of such moulded resin products are extremely diversified, it is preferred to arrange them to a certain size and state form etc. by cutting or crushing in order to make the treatment that will be discussed below, smoother.

These moulded resin products, with an arranged or not arranged form, are submitted to a degradation treatment (degradation reaction), together with 1-100 times their weight of methanol or ethyleneglycol, and preferably together with 3-50 times their weight and particularly 5-50 times their weight of methanol or ethyleneglycol. The reason for the regulation of the methanol quantity or ethyleneglycol quantity is in the first place due to the problem of the size of the reactor, and on the other hand, also due to the point of the efficiency of recovery of the dimethylterephthalate, and of the purity of the recovered dimethylterephthalate.

The reaction with methanol or ethyleneglycol usually may be carried out without a catalyst, but if it is necessary for improvement of the reaction velocity, or, on the other hand, for improvement of the purity of the product, or for improvement of the colour of the product, a catalyst may be added. As such catalysts, compounds of metals such as iron, cobalt, nickel, copper, zinc, silicon, tin, magnesium, calcium, sodium and potassium, are preferred. Particularly oxides, hydroxides, and lower carboxylates are preferred. As oxides, for instance, ironoxide, cobaltoxide, copperoxide, siliconoxide, magnesiumoxide, calcium-

oxide, sodiumoxide and potassiumoxide can be mentioned. Moreover, in addition, phosphoric acid, pyrophosphoric acid, boric acid, boric acidanhydride and salts thereof can be used.

A good quantity of use of these catalysts is 0.001-10 wt% to the methanol or ethyleneglycol; and preferably 0.01-5 wt%.

In most cases, a high reaction temperature is preferred, because in general the reaction velocity increases when the reaction temperature rises, but in this invention, this is not preferred, because not only methanol and ethyleneglycol are consumed in side reactions such as ether formation in the temperature range above 3000 C, but also burning of the raw materials occurs. This is not wanted, because for instance the rate of recovery and purity of dimethylterephthalate decline when burning of the raw materials occurs. Consequently, the preferred range of the reaction temperature is 150-3000 C, and particularly the range of 170-2700 C.

The reaction time is settled in connection with the reaction temperature, and it is sufficient when a reaction of 5 hours is carried out at 1900 C, and 1 hour at 2500 C.

In the execution of the depolymerization with methanol, the obtained reaction product is a mixture of dimethylterephthalate and methanol and other methanol soluble matter, that contains undissolved matter, but in the presence of methanol, the dimethylterephthalate is separated from this reaction mixture. It is particularly preferred to carry out the recovery by hot filtration of the methanol solution of dimethylterephthalate. If necessary, the adsorbed dimethylterephthalate is recovered from the undissolved matter by rinsing it with methanol. The processes of filtration and rinsing are preferably carried out at 500 C or higher to the reaction temperature. Particularly preferred is execution in the range from the boiling point of methanol to the reaction temperature.

The thus obtained methanol solution of dimethylterephthalate is simply cooled, or, if necessary, the methanol is removed by distillation, and the crude dimethylterephthalate is crystallized and recovered.

The quantity of methanol that is removed in this case is such that the residue contains 1-95 wt%, and preferably 5-90 wt%, and still more preferred 10-90 wt%, methanol. By this removal of

methanol and by crystallization, the yield of dimethylterephthalate rises, and simultaneously, the purity of the product rises, and hereby, the quality, for instance the colour and the softening point, of the polymers wherein the said dimethylterephthalate is used, are improved. Moreover, the purification in the above mentioned purification process is simple, and creates an important advantage for the industry.

By execution of distillation and recrystallization from methanol of the thus obtained crude dimethylterephthalate, dimethylterephthalate with an extremely high quality is recovered.

Moreover, in the case that depolymerization is carried out with ethyleneglycol, the obtained reaction product is a mixture of esters of terephthalic acid and oligomers thereof (below abbreviated to BHET), ethyleneglycol, and other matter that is soluble in ethyleneglycol, that also contains insoluble matter, and from such mixtures, BHET is isolated in the presence of ethyleneglycol. It is particularly preferred to filter the ethyleneglycol solution of BHET while it is hot. If necessary, the BHET that has been adsorbed to insoluble matter, may be washed with ethyleneglycol, and be recovered, and in addition, adsorbed BHET and ethyleneglycol may be recovered by pressure or by the operation of centrifugal separation. Such operations are preferably carried out in a temperature range of reaction temperature to 200 C. The thus obtained ethyleneglycol solution of BHET is simply cooled, or, if necessary, BHET is recovered by removal of the ethyleneglycol by distillation. Or it is, without having been recovered, simply recovered as dimethylterephthalate by methanolysis.

From the viewpoint of the purity of the final product, it is preferred that BHET is recovered and purified, and that subsequently methanolysis is carried out, but from the viewpoint of production costs, it is preferred to simply submit the crude BHET to methanolysis.

The ethyleneglycol solution of BHET after termination of the decomposition reaction is a system that contains an extremely large variety of insoluble matter, for instance nitrogen containing compounds such as polyamide and amines with a low molecular weight, and dyes and pigments, and various additives.

---- the ethyleneglycol solution of BHET, free ethyleneglycol

is removed by distillation, and the concentration by weight of free ethyleneglycol in the system 1-95 wt%, preferably 5-90 wt%, and most preferred 10-90 wt%. The thus prepared ethyleneglycol solution of BHET may be simply offered as such to methanolysis, but methanolysis after isolation by crystallization is preferred.

Moreover, it is not particularly necessary that the ethyleneglycol that is used in this invention has a high purity, and it may contain a small quantity of insoluble matter, such as aqueous BHET. Moreover, the above mentioned reaction may be carried out in the co-presence of compounds such as hydrocarbons, ethers, ketones and esters, that are liquids under the reaction conditions, and do not hamper the reaction.

The methanolysis of BHET is carried out in the presence of 1-100 times, and preferably 1-50 times, and even more preferred 1-30 times (by weight) as much methanol as BHET. The reaction can be carried out without a catalyst, but for the reaction velocity and the purity of the dimethylterephthalate, a catalyst is added if necessary.

As such catalysts, compounds of metals such as Li, Na, K, Mg, Ca, Sr, Ba, Ti, Zr, Cr, Mo, W, Mn, Fe, Co, Ni, Cu, Zn, Al, Si, Ge, Sn, Pb, La and Ce, and particularly compounds such as oxides, lower carboxylates, alcoxides and hydroxides, can be mentioned. Or besides, phosphoric acid, boric acid and sulfonic acid etc. can be used. The quantity of catalyst that is used preferably is 0.001 wt% to 10 wt% to the crude BHET. The reaction temperature is ca. 70 to ca. 300°C, and preferably ca. 70 to ca. 250°C, and more preferred is the temperature range of ca. 70 to 200°C. The higher the temperature, the higher the reaction velocity, but when it is too high, decomposition of methanol occurs, and this has an unwanted influence of the purity of the product.

The reaction time depends in general on the reaction temperature, kind of catalyst, and quantity of use thereof, but as a rule, 10 hours is sufficient at a reaction temperature of 150°C, and 5 hours at 200°C. Usually, about half of the above mentioned reaction times is possible in the case that a catalyst is used.

It is not necessary that the methanol that is used in this

invention is pure, it may contain a small quantity of ethylene-glycol, water and dimethylterephthalate etc.

The dimethylterephthalate that is obtained by simply cooling the reaction mixture that is obtained by methanolysis, or, if necessary, by removing a part of the methanol by distillation, is recovered. The treatment in this case is carried out, succeeding the purification when the moulded resin product has been depolymerized with methanol.

Or the above mentioned purified or crude dimethylterephthalate may also be converted to terephthalic acid by execution of hydrolysis.

Below, this invention is explained further by examples of execution, but this invention is not limited to the below mentioned examples of execution, in so far as the range of the essentials thereof is not exceeded.

#### Example of execution 1.

A mixture of 200 g cotton-Tetoron® (35/65) fabric, 50 g nylon 6 socks, 50 g worsted acryl and 50 g cotton fabric were brought in a 1 l autoclave, together with 500 g methanol, and reacted 5 hours at 2300 C, and filtered while still hot, 1500 C, and the residue was washed with 50 g methanol. 300 g methanol was evaporated, and the crystals that had separated out after cooling to room temperature, were filtered off, and recrystallized from 1000 g methanol. When the obtained dimethylterephthalate was isolated by distillation, 90 g fiber grade dimethylterephthalate was obtained.

#### Examples of execution 2-10.

The reaction was carried out in the same way as in example of execution 1, but with addition of 50 g of the catalysts that are shown in table 1, and subsequently, the same treatment as in example of execution 1 was carried out, with the exception that reaction temperature and time were the values that are shown in table 1. Table 1 also shows a summary of the results.

Table 1.

example of execution	catalyst	reaction temperature/time	quantity of dimethylterephthalate
2	magnesiumoxide	200 (0C)/2 (hr)	97 (g)
3	calciumacetate	180 /5	98
4	zinc oxide	250 /1	100
5	cobaltacetate	200 /2	95
6	iron oxide	210 /3	94
7	phosphoric acid	200 /2	96
8	boric acid	230 /2	93
9	calciumoxide	200 /1	99
10	copper oxide	200 /3	96

## Example of execution 11.

500 g cotton-Tetoron (R) (35/65) fabric, 100 g nylon 6 socks, 100 g worsted acryl and 100 g cotton fabric were brought in a 3 l autoclave, together with 1000 g ethyleneglycol, and reacted 3 hours at 2300 C, and filtered while still hot, 1500 C. The undissolved matter was washed with 200 g ethyleneglycol, and this was combined with the mother liquor. From the mother liquor, 700 g ethyleneglycol was flash distilled, and the residue was cooled and separated out, and 420 g crude BHET were recovered by filtration.

After 3 hours reaction of 100 g of this BHET with 500 g methanol and 0.5 g calciumhydroxide(?) at 1500 C, 200 g methanol were removed, and subsequently this was cooled, the dimethylterephthalate that separated out was filtered off, and again recrystallized from 900 g methanol, and thereafter distilled. 62 g fiber grade dimethylterephthalate were obtained.

## Examples of execution 12-19.

These were carried out in the same way as example of execution 11, but as a whole, on 1/5 of the scale. In the ethyleneglycolysis, however, 1 g catalyst was used, and they were carried out with the reaction temperatures and times that are shown in table 2.

Methanolysis and purification were carried out in the same way as in example of execution 11. The obtained dimethylterephthalates were in all cases fiber grade ones. The results are shown in table 2.

Table 2.

example of execution	catalyst	reaction temperature/time (°C) / (hr)	quantity of dimethylterephthalate (g)
12	iron oxide	200 /2	53
13	magnesiumoxide	180 /5	61
14	zinc acetate	220 /2	56
15	phosphoric acid	200 /1	59
16	bariumoxide	200 /2	54
17	cerium acetate	200 /1	63
18	cobalt acetate	180 /5	61
19	copper oxide	200 /3	52

## Examples of execution 20-25.

By execution in the same way as in example of execution 11, with the exception that 100 g BHET, that had been obtained in the same way as in example of execution 11, was used and that catalyst, reaction temperature and reaction time were changed as is shown in table 3, dimethylterephthalate was recovered. The results are shown in table 3. All dimethylterephthalates were fiber grade ones.

Table 3

example of execution	catalyst/ quantity (g)	reaction temperature/time (°C) / (hr)	quantity of dimethylterephthalate (g)
20	lead acetate/0.5	150 /3	60
21	cobalt acetate/0.5	150 /3	58
22	p-toluenesulfonic- acid/1.0	180 /3	59
23	zinc acetate/0.5	180 /3	59
24	iron oxide/1.0	180 /3	63
25	no catalyst	200 /3	57

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